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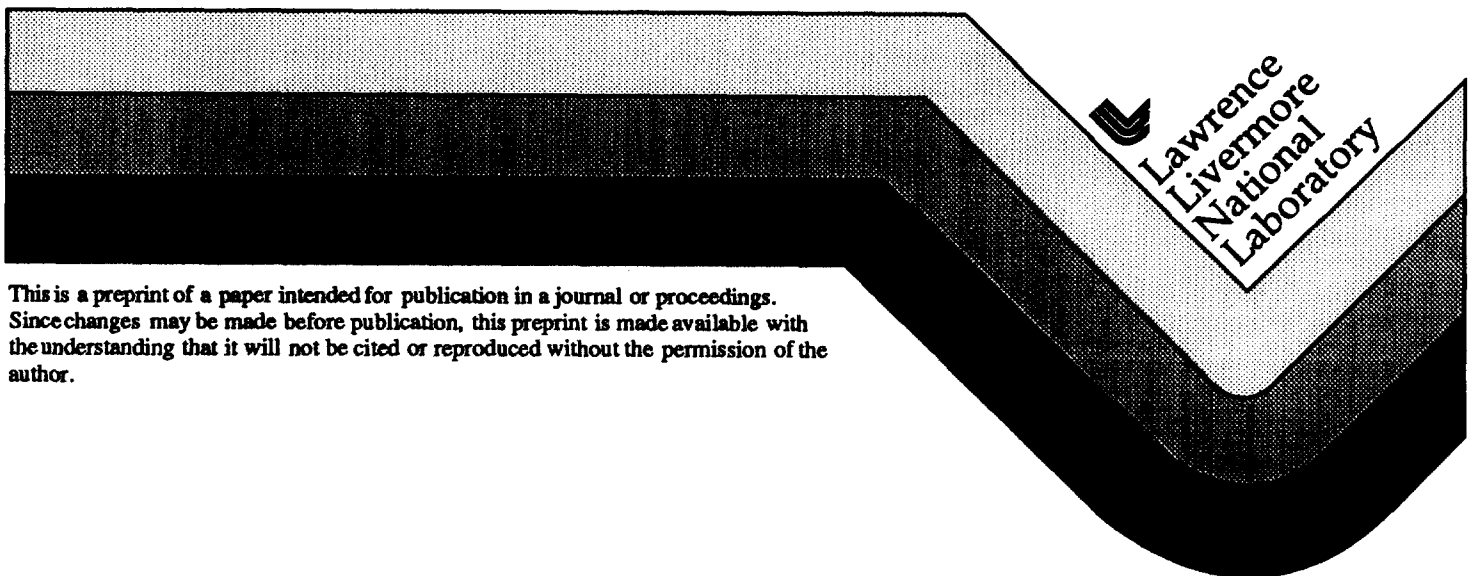
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Dumping Pump and Treat: Rapid Cleanups Using Thermal Technology

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**Dumping Pump and Treat:
Rapid Cleanups Using Thermal Technology**

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**Lawrence Livermore National Laboratory
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The Problem

Underground spills of volatile hydrocarbons are often difficult to clean up, especially if the contaminants are present in or below the water table as a separate liquid-organic phase. Excavating and treating the contaminated soil may not be practical or even possible if the affected zone is relatively deep. Merely pumping groundwater has proven to be ineffective because huge amounts of water must be flushed through the contaminated area to clean it; even then the contaminants may not be completely removed. Due to the low solubility of most common contaminants, such pump and treat systems can be expected to take decades to centuries to actually clean a site.

Today, many sites are required to pump and treat contaminated groundwater even though there is no expectation that the site will be cleaned. In these cases, the pumps simply control the spread of the contaminant, while requiring a continuous flow of money, paperwork, and management attention. Although pump and treat systems are relatively inexpensive to operate, they represent a long term cost. Most importantly, they rarely remove enough contaminant to change the property's status. Although a pump and treat system can offer compliance in a regulatory sense, it doesn't solve the site's liability problem.

Thermal methods promise to solve this dilemma by actually cleaning a property in a short time period, thus limiting the period of liability. This may involve cleaning a site to closure during the initial contaminant-removal phase, or removal of the majority of the contaminant so that natural processes such as bioremediation can return the site to pristine condition over a period of years, without further owner intervention. Today's regulatory environment encourages this approach through efforts such as the brownfields initiatives. In either case, this requires a strong commitment on the part of the site owner. Most if not all the cleanup occurs within the first year or so, and nearly all the cost. In our experience, the total cleanup cost is still significantly smaller than with conventional methods. The real benefit is the cleanup and thus the removal of liability within a realistic time frame.

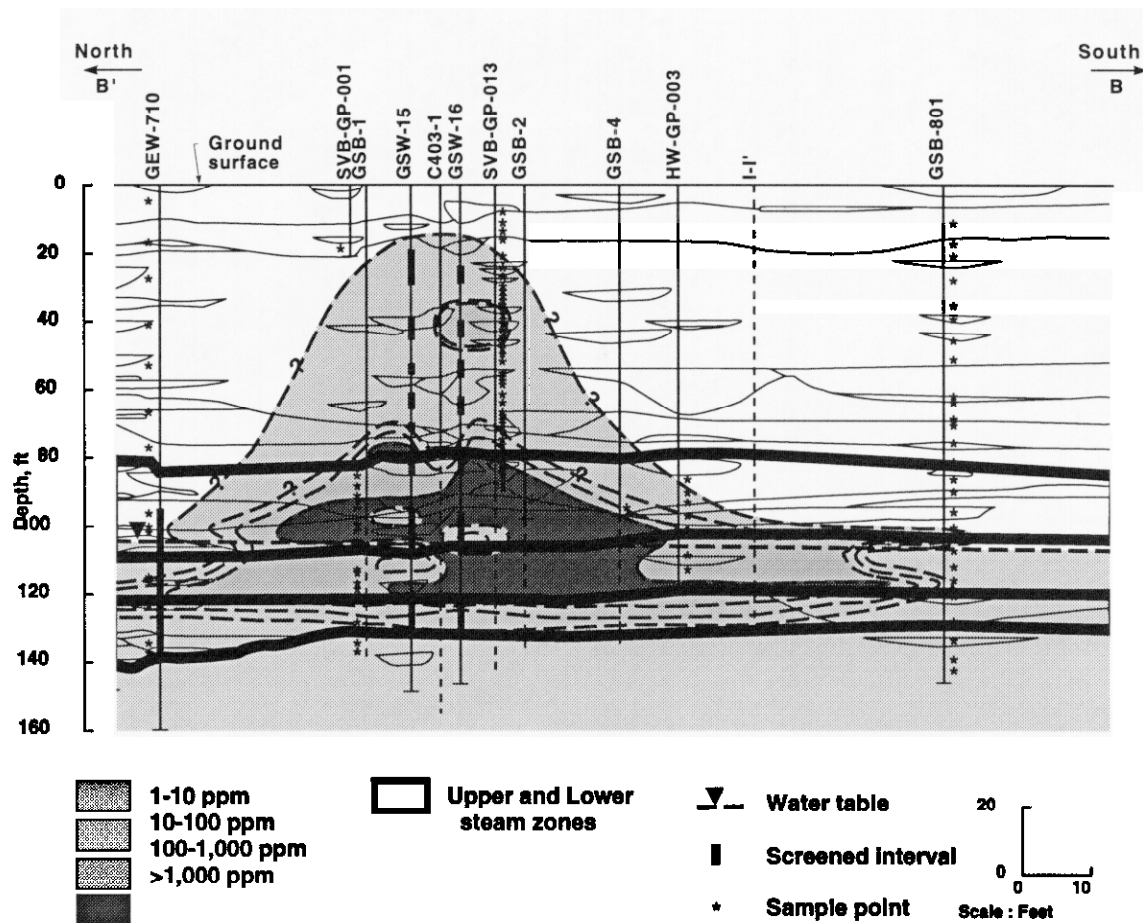
Why Use Heat?

The rationale behind using heat to speed groundwater cleanup is readily apparent; just as any of the more familiar cleaning tasks are accomplished more rapidly with hot water, the use of steam or electrical heating can dramatically increase the rate of soil and groundwater cleanup. Thermal remediation methods are effective due to a variety of factors; increased contaminant volatility, rapid mass transfer, diffusion and evaporation, lower viscosity of water and

contaminants, decreased sorption, boiling of the formation, and overall increase in the speed of chemical reactions. Lawrence Livermore National Laboratory has collaborated with the University of California at Berkeley (UCB) College of Engineering in the development and demonstration of thermal methods for the rapid cleanup of underground volatile contaminants. We have developed a set of methods that can be used over a period of six months to one year to complete the cleanup of sites that routinely take decades to clean today. The Department of Energy's Office of Environmental Restoration and Waste Management sponsored a full-scale demonstration of this technique at the LLNL gasoline spill site. The most significant aspect of our work has been to demonstrate that these methods can be used safely, effectively, and that they can achieve the desired result (site closure and de-listing) in a short period of time. The focus of our effort has been in replacing pump-and-treat technology.

Dynamic Underground Stripping: A Worked Example

LLNL has recently completed the cleanup and closure of a moderate-sized spill site in which thermal cleanup methods, and the associated control technologies, were used to remediate over 10,000 gallons of gasoline trapped twenty feet below the standing water table (Newmark, 1992, 1994a). The spill originated from a group of four underground tanks, from which an estimated 17,000 gallons of gasoline leaked sometime between 1952 and 1979. The gasoline penetrated the soil, eventually reaching the water table, where it spread out. Subsequent rise in the water table due to changes in agricultural water use trapped considerable free product below the water table. Previous characterization results were combined with an extensive set of measurements taken during our installation of 22 process and monitoring boreholes to estimate that 6200 gallons of gasoline were present (both above and below the water table) within our target treatment area (Figure 1). Gasoline trapped up to 30 ft below the water table was there due to a rise in the water table after the spill occurred, with the gasoline held below water by capillary forces in the soil. Groundwater contamination extended about 200 m beyond the central spill area (Figure 2). The soils at the site are alluvial, ranging from very fine silt/clay layers to extremely coarse gravels, with unit permeabilities ranging over several orders of magnitude. There are two principal permeable zones, one above and one below the water table. The site was prepared for long-term groundwater pump-and-treat with vapor extraction; recovery rates prior to thermal treatment were about 2.5 gal/day (Figure 3).



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Figure 1. Soil concentrations of total petroleum hydrocarbons measured in pre-operations core samples. Note position of the water table, at 105 ft.

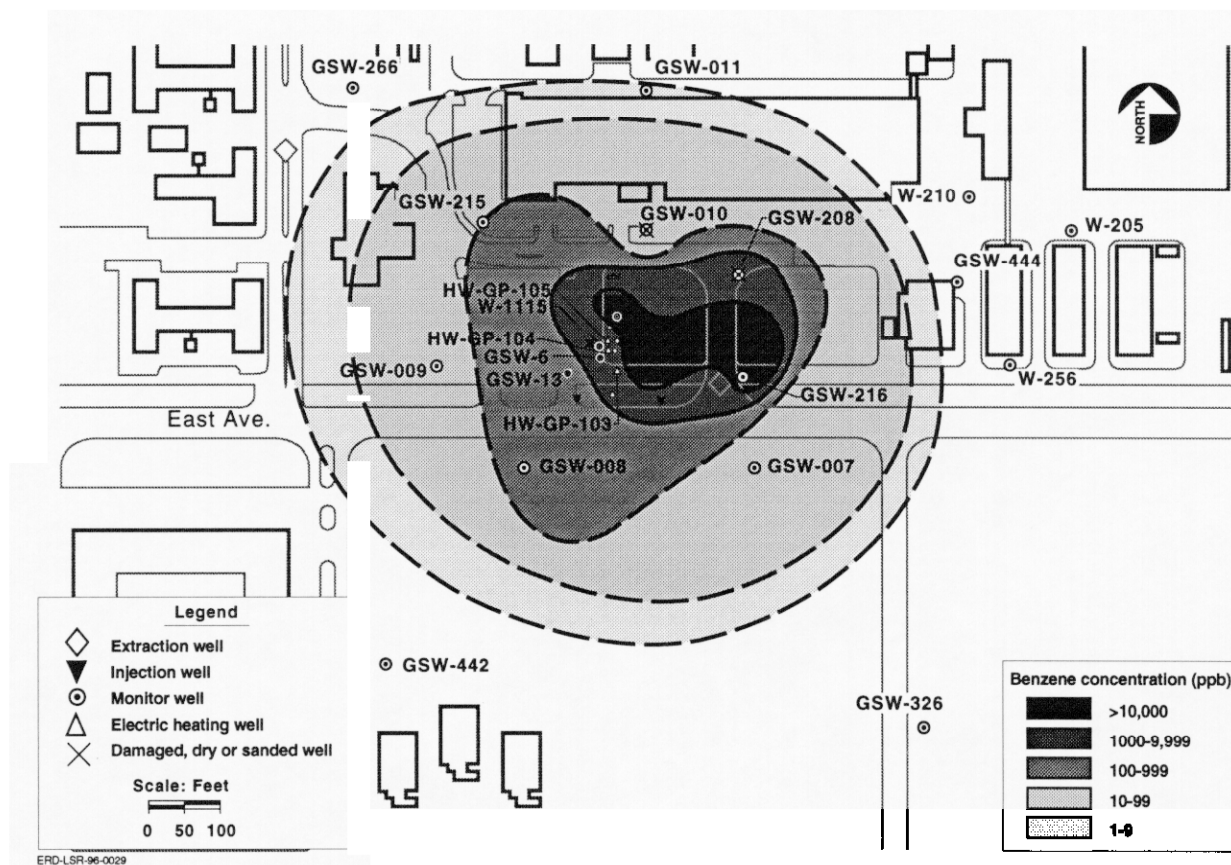


Figure 2. Maximum historical ground water benzene concentrations prior to remediation in HSU-3 (the target hydrostratigraphic zone)(from Happel et al., 1996).

The targeted volume was intended to include all of the free-phase gasoline at the site. Its shape is that of a distorted cylinder about 120 ft. in diameter and 80 ft high, extending from a depth of 60 ft to a depth of 140 ft. The water table is located at 100 ft. Later results indicated that two small areas of gasoline probably existed outside the treatment area, possibly from separate spills. Six steam injection/electric heating wells were placed to surround the free product in an irregular circle determined by the shape of the free product; and three additional electric heating wells were placed near the center of the spill. These were not part of the original design, but were required when the free-product zone was discovered to be larger than anticipated during the drilling of the injection wells. Each injection well was initially center-punched with a small-diameter hole for characterization. The discovery of unexpected free product in two of them had minimal impact; the holes were completed as monitoring locations and new injection wells drilled further from the spill center. Eleven monitoring/imaging wells were placed within and outside the target area to provide control of the heating processes. In an operational period of 1 year, followed by a monitoring period of two years, a volume of soil of approximately 100,000 yd³ was cleaned and

extraction/treatment operations were terminated. Following removal of more than 99% of the contaminant, and achievement of Maximum Contaminant Limit (MCL) levels in groundwater for five of the six contaminants, the site will now be passively monitored under an agreement with the California Regional Water Quality Control Board (RWQCB), California EPA's Department of Toxic Substances Control (DTSC), and the Federal EPA Region 9. This cleanup was achieved using a group of cleanup methods collectively called Dynamic Underground Stripping.

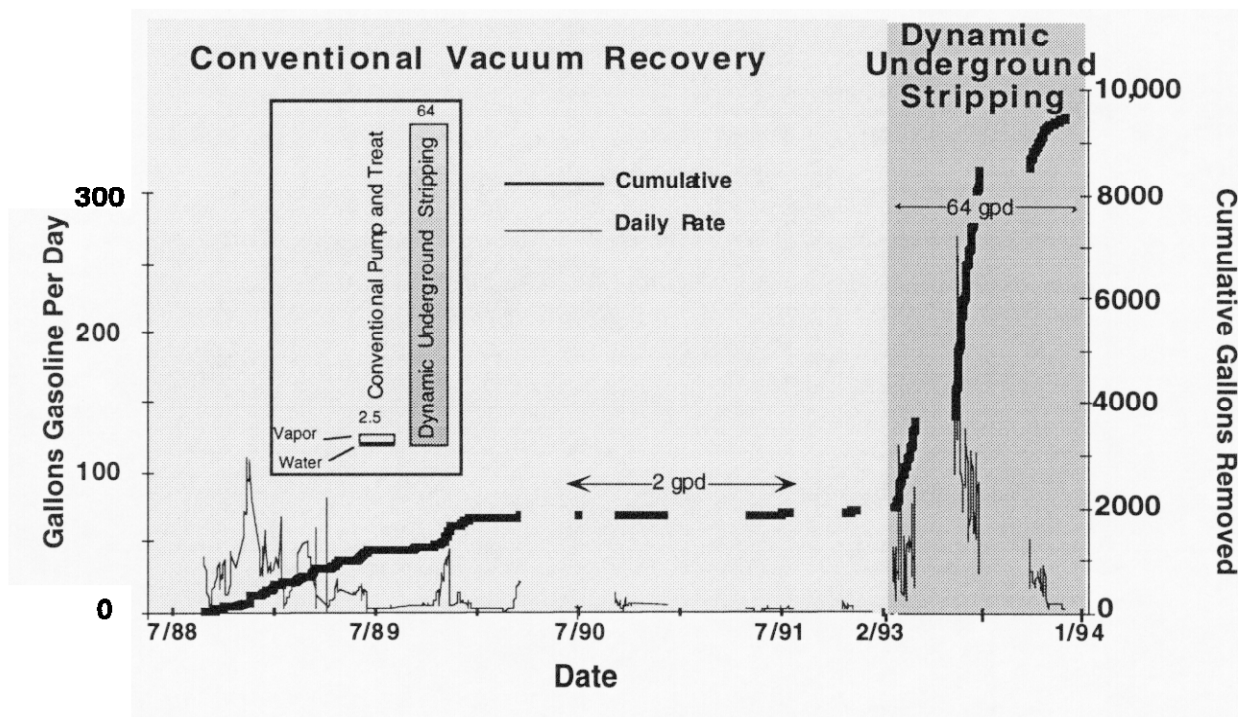


Figure 3. Recovery history of the gasoline spill site. Vacuum extraction began in 1988; after initial high rates, recovery leveled off at about 2 gpd. Groundwater extraction began early in 1993; recovery rates increased to 2.5 gpd. Dynamic Underground Stripping recovery operations began in February, 1993. Operating for 21 weeks over the period of a year, recovery averaged 64 gpd.

Results of first full-scale test

The first full-scale test at the LLNL gasoline site was extremely successful. Process results completed in June 1993 indicated that for the removal of contaminant, the process is 50 times as effective as the conventional pump and treat process now being used at 300 designated Superfund Sites, and is 10 times as effective as another enhanced new method (pump and treat with vacuum extraction). During 21 weeks of operation, the technique removed more than 7600 gallons of an estimated 6200 gallons of gasoline trapped in soil both above and below the water table, with separate phase contamination extending to >120 ft deep. The

maximum removal rate was 250 gallons of gasoline a day. The process was limited only by the ability to treat the contaminated substance. Actual field experience indicates that the process costs \$65 a cubic yard. Approximately 100,000 yd³ were cleaned.

Dynamic Underground Stripping is based on three technologies

Dynamic Underground Stripping combines two methods to heat the soil, vaporizing trapped contaminants (Figure 4). Permeable layers (e.g., gravels) are amenable to heating by steam injection, and impermeable layers (e.g., clays) can be heated by electric current. These complementary heating techniques are extremely effective for heating heterogeneous soils; in more uniform conditions, only one or the other may be applied. Once vaporized, the

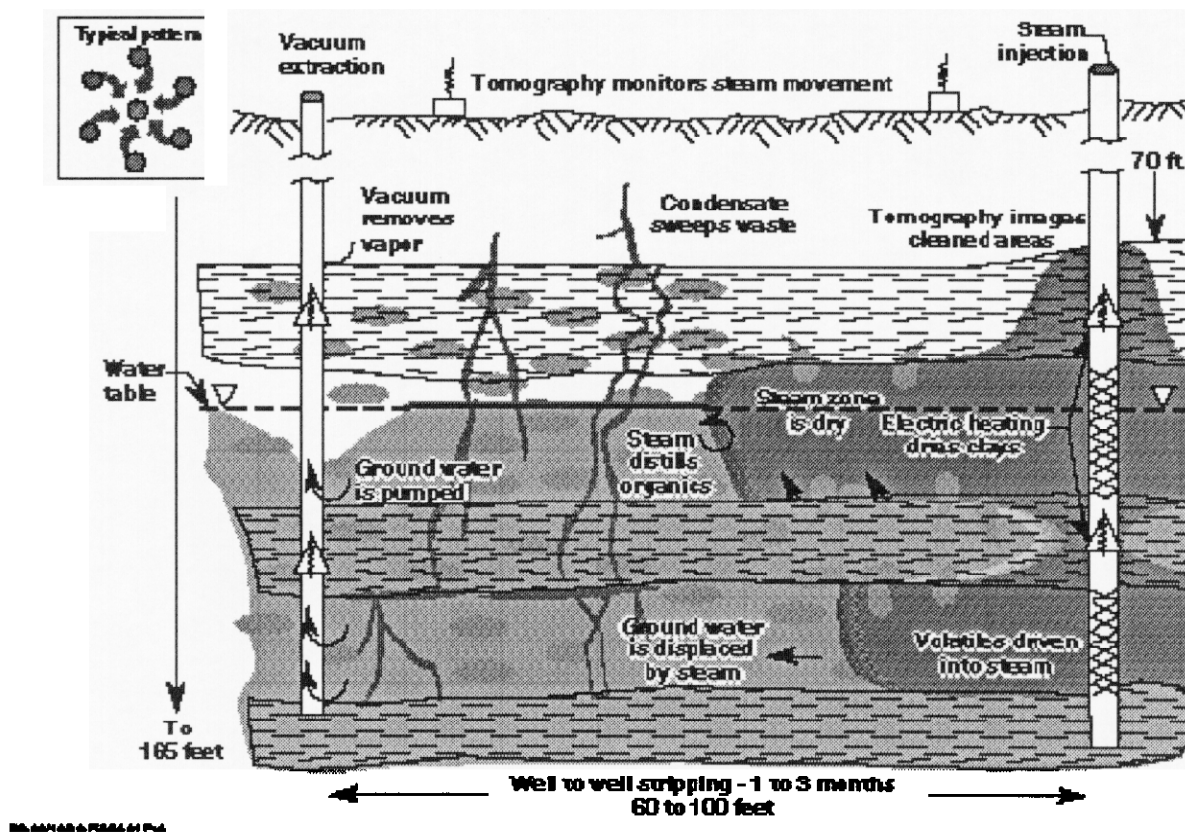


Figure 4. In Dynamic Underground Stripping, steam drives contaminated water toward extraction wells and then heats the soil to distill organic compounds. Electrical heating dries and distills contaminants from impermeable clays that the steam cannot readily penetrate. Geophysical techniques monitor the process. The method operates both above and below the water table and is particularly economically attractive for removing separate phase contaminants.

contaminants are removed by vacuum extraction. All these processes - from the heating of the soil to the removal of the contaminated vapor - are monitored and guided by underground imaging, which assures effective treatment through *in situ* process control.

Steam Injection and Vacuum Extraction: Injection wells drilled around an area of concentrated contamination are used to supply both steam and electric current. Extraction wells placed near the center of the contamination are used to extract the contaminant. The steam is pumped in through the injection wells and advances in a wall, or front, toward the extraction wells. Concurrently, groundwater is pumped and vapor is extracted from the extraction wells. As the steam front advances, the permeable soils are heated to the boiling point of water (100°C), and volatile organic contaminants are vaporized from the hot soil. After the steam front reaches the extraction wells, steam injection is stopped; vacuum continues to be applied at the extraction wells. The lowered vapor pressure (resulting from the applied vacuum) forces the contaminants to boil and the concentrated contaminant-carrying vapor is then pumped to the surface and treated. When the steam zone collapses, groundwater reenters the treatment zone. The steam injection/vacuum extraction cycle is repeated, and additional contaminants are vaporized and removed.

Electrical Resistance Heating: Electric current is used to heat the impermeable soils. It operates on the same principle that makes a heating coil work - heat builds up in a conductor that resists current flow. For this technique, the clay itself supplies the resistance. In the steam injection wells, electrodes are sunk into the ground. Each electrode supplies several hundred amperes of current at up to 600 V, heating the impermeable clays. Water and contaminants trapped in these (relatively) conductive regions are vaporized and forced into the steam zone for vacuum extraction.

These combined heating processes achieve a hot, dry zones surrounded by cool, damp, untreated areas. Electrical heating and steam injection are repeated as long as underground imaging shows that cool (and therefore untreated) regions remain.

Underground Imaging and Process Control: Several geophysical techniques are used to monitor the underground movement of steam and the progress of heating, including temperature measurements and electrical resistance tomography. Monitoring the progress of the heating fronts during operations allows the process engineer to ensure that all the soil is treated. If the monitoring indicates a region of cool, contaminated soil, the operational strategy can be altered to treat the offending area. Temperature measurements made in monitoring wells in the treatment area reveal details of the complex heating phenomena in the individual soil layers. Electrical resistance tomography provides near-real-time images of the

underground processes between wells. Because soil electrical properties vary with temperature, soil type and fluid saturation, electrical measurements can map the progress of the steam front and the heated zones. They are also useful for characterizing a given site and for predicting steam pathways. Tiltmeters are used to track the movement of the steam front; these devices are capable of detecting very small angular deformations in the ground surface that results from subsurface pressure changes, such as those that occur with the movement of the steam front.

Operations

The first application of Dynamic Underground Stripping was conducted in three phases. The electrical preheat and first steam pass which comprise the first phase and the second steam pass were funded and conducted as research, development and demonstration; the final heating and extraction were conducted under the auspices of the main LLNL site cleanup.

Electrical Preheating

Electricity preferentially flows in areas of high conductivity; the hotter the soil, the higher the conductivity. Initially, the clays are much more conductive than the gravels; preheating these zones by about 20 ° C ensures that the clay-rich zones remain more conductive than the gravels zones, even after steam injection. In November and December 1992, the electrical heating system operated at a maximum power of 800 kW, heating the target volume clay layers in some areas to temperatures exceeding 70° C.

First Steam Pass

Steam injection began in early February, 1993. For 37 days, a gas-fired boiler of ~8 MW put out 11,000 kg/h (190 liters/min) of steam. The spreading steam rapidly heated the permeable layers to the boiling point of water (Figure 5). Initial steam breakthrough to the extraction wells occurred in only 12 days; each subsequent breakthrough occurred sooner as the formation gained heat. This made day-to-day process monitoring critical to assure that the correct amount of steam was injected to drive contaminant to the center without adding excessive amounts of steam outside the pattern (such as driving steam below the adjacent Sandia Livermore site, which we had agreed not to do). A small fraction (about 15%) of the free-product gasoline was pushed ahead of the steam front and recovered as liquid; most of the gasoline was removed as vapor after the steam zone was fully established.

Each of the twelve injection ports (two each in six wells) would inject a different amount of steam at a given pressure, ranging from 600 lb./hour to one well that would apparently have taken the entire output of the boiler if permitted. This large range is expected in such a heterogeneous site, but requires that the location and size of the steam zones be measured *in situ*, not merely calculated from injection volumes.

Temperatures were measured using fixed thermocouples and in continuous logs using an infrared-sensor system in the 11 monitoring/imaging wells. Temperature gradients of up to 100°C were observed over just a few feet depth during initial steam injection; the temperature logs provided the most accurate measurements of the vertical distribution of the steam at specific locations throughout the site (Figure 5).

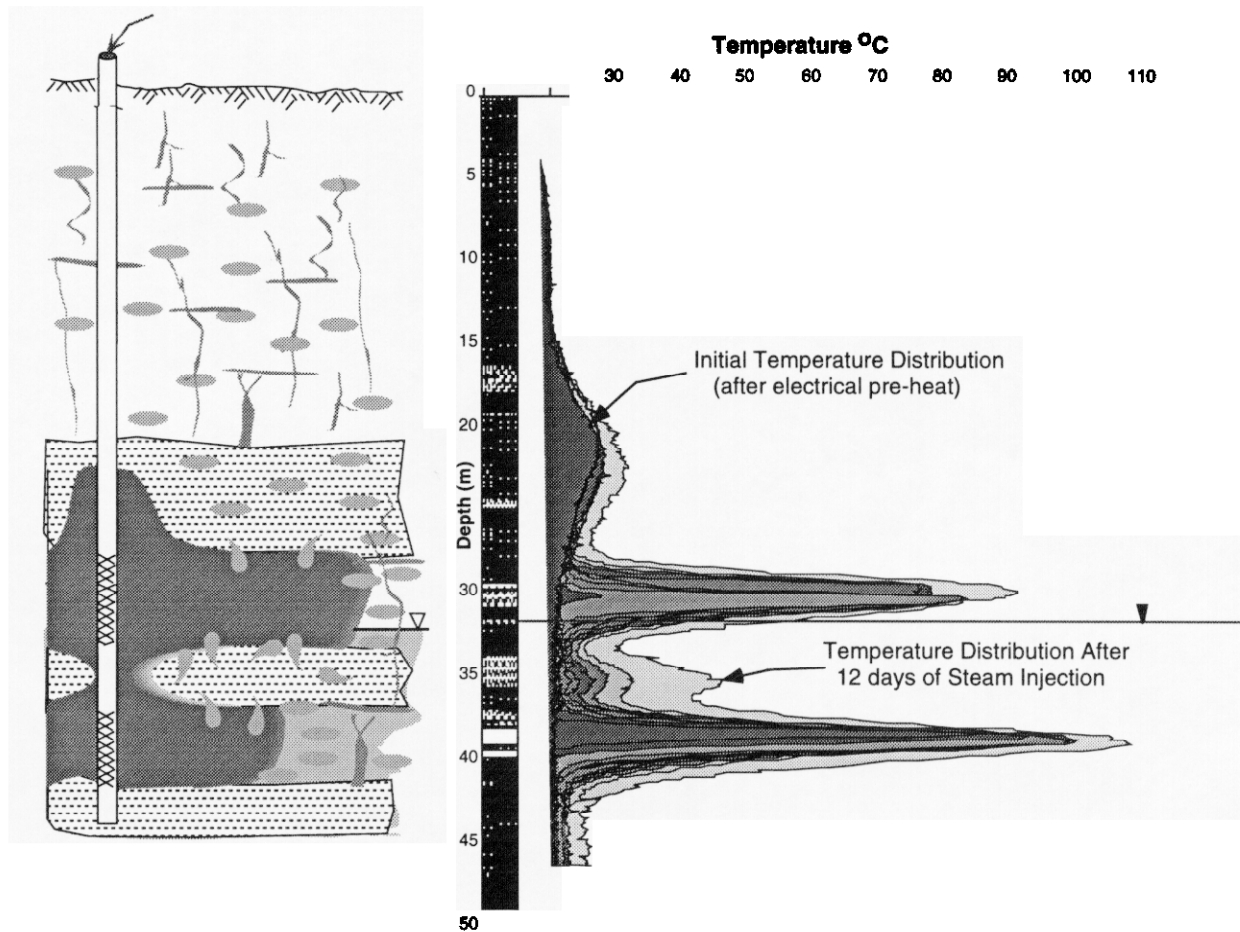


Figure 5. Temperatures logged over the first 12 days of steam injection in a borehole between steam injection wells reveal steam penetration over time. Steam initially penetrates the more permeable gravel units; temperatures increase in intervening clay-rich units by a combination of conduction and convection.

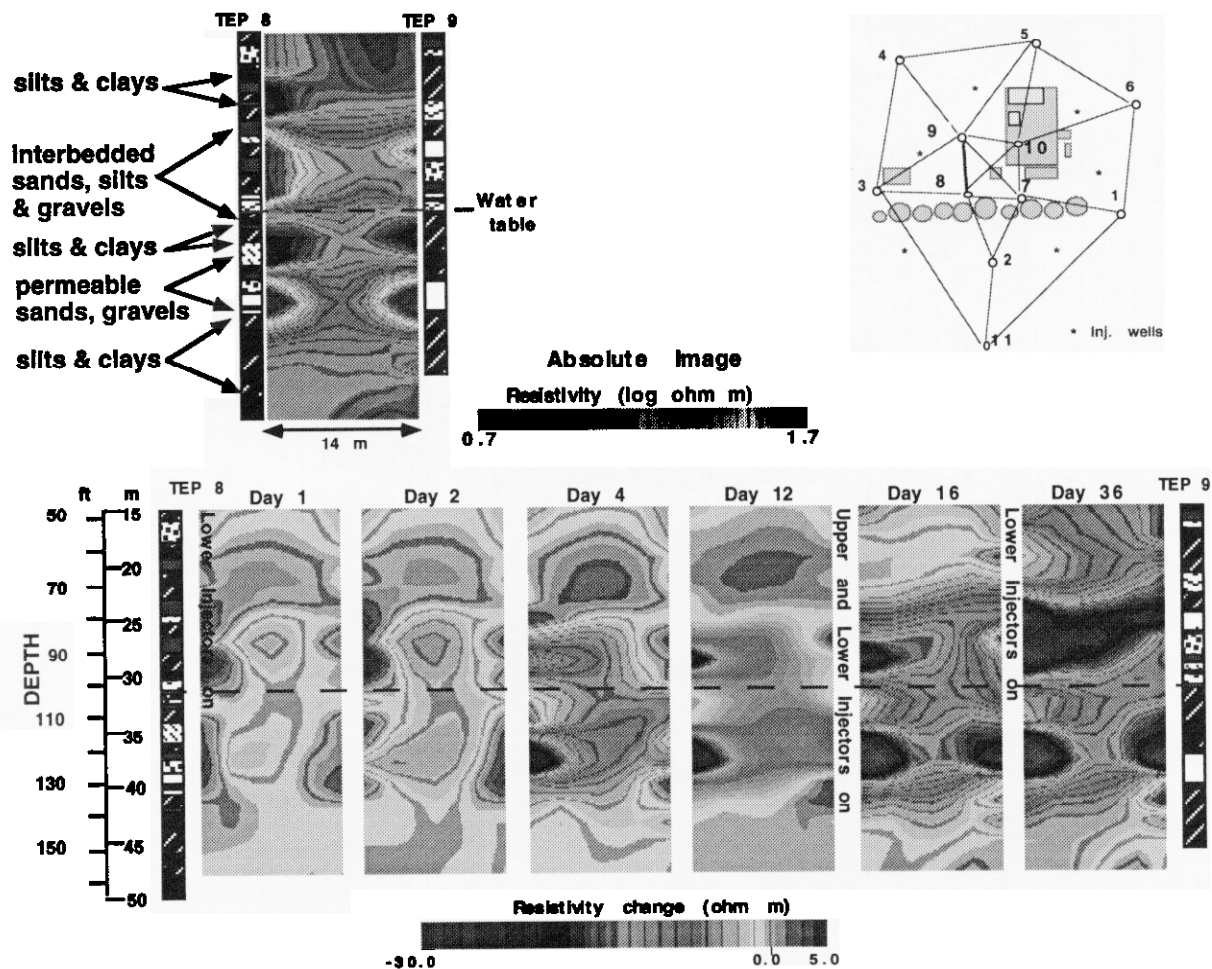


Figure 6. Electrical resistance tomography (ERT) images. Top: ERT absolute images reveal the continuity of soil units across image planes. The resistive units correspond to the more permeable sand and gravel zones; the conductive units correspond to the clay-rich intervals. (The apparent pinching-out of units in the center of the image is due to the increase in resolution radius toward the center of each image). Bottom: ERT difference images show the progress of the steam fronts across the image plane, starting from the first day of steam injection. This image plane (between wells TEP8 and TEP9) is located about 6 m from the nearest injection well, and is oriented nearly perpendicular to a line linking it and the extraction wells. Electrical resistivity decreases within hours of the start of steam injection. By the end of the first steam pass (Day 36), both the upper and lower steam zones are at or near steam temperature, with primarily conductive heating occurring in the neighboring clay-rich units. The preferential steam paths closely follow the more resistive units observed in the absolute images (from Newmark, 1994b)

Between the wells, electrical resistance tomography (ERT) proved to be a rapid and accurate way to map steam progress at 1-2 meter resolution, providing actual images of the heated zones by comparing the electrical resistance distribution prior to heating to that afterwards (Figure 6). These images showed a number of areas where steam was moving vertically in the formation that were not detected by the temperature logs. The total-cycle time to obtain and process the data was less than one day. This made ERT the principal control method, and

morning operations meeting decisions on steam injection rates were based principally on ERT images from the previous day. The combined ERT/temperature wells were placed to allow optimal monitoring of the interior of the treated zone (extending about 30 ft outside the ring defined by the steam injection wells) and lower resolution monitoring of the surrounding area.

Surface-implanted tiltmeters were arranged in a larger array to monitor the full extent of the steam zone outside the treated area. These were used to measure the slight deformation in the ground surface that occurs when a pressure transient was induced into the steam zone by shutting off an injection well for 1 hour. Maps of the aerial extent of the steam zone emanating from each well could be obtained, particularly for the lower steam zone (located below the pre-steam water table). This technique was extremely effective in mapping the lateral spread of steam and the development of any preferential steam pathways.

Evaluation of the gasoline concentration in the effluent from the extraction well proved difficult. Most of the gasoline was removed in the vapor phase, and much of that is condensed along with a large amount of water in the heat exchanger. The addition of an oil-water separator on this part of the effluent stream allowed an accurate determination of the condensed portion of the flux by simple volume measurement. The remaining dried, cooled vapor was burned in two internal combustion engines; the flux of gasoline in this stream was highly variable, as a function of the amount of steam in the injection wells, total vacuum applied, and time of day (temperature of the heat exchanger). A series of continuous chemical sensing systems was employed to measure this flux and to allow the same level of control for the chemical extraction rate as was obtained for the thermal injection systems.

Because of the cost and hazards associated with sampling and analysis, off-line vapor samples were only collected once or twice daily. This sampling frequency provides somewhat limited insight into the Dynamic Underground Stripping process, and cannot provide sufficient data for detecting short-term fluctuations in system performance or for real-time optimization and control of the system. A series of continuous in-line chemical sensing systems was employed to measure this flux and to allow the same level of control for the chemical extraction rate as was obtained for the thermal injection systems. These included a standard fourier transform infrared (FT-IR) spectrometer equipped with a gas sample cell, an automated gas chromatograph (with PID detection), and the experimental Differential Ultraviolet Absorption Spectroscopy (DUVAS) system. The trends indicated by the in-line sensors were in agreement with standard off-line laboratory analyses, and were obtained continuously in near or real-time (Figure 7a). Continuous monitoring allowed transient events and mid- to long-term trends in the extraction process to be measured. For example, the DUVAS data showed

significant diurnal fluctuations in the absorption of total aromatic compounds; these fluctuations corresponded with recorded variations in ambient temperature and changes in the pressure and flow rates within the vapor extraction system (details of the sensor responses can be found in Newmark, R.L (ed.), 1994a)(Figure 7b). The correlation between ambient temperature and sensor response led to an analysis of the vapor system's efficiency. The fluctuations appear to be caused by changes in condensation efficiency resulting from variations in ambient temperatures (higher condensation rates during the cooler nighttime temperatures.) This explanation also resolved the apparent scatter between the contaminant concentrations measured in the morning and afternoon vapor samples (the morning values showed significantly lower concentrations than the afternoon samples). Thus, the in-line sensors, due to their high sample frequency, revealed trends and provided a context in which to interpret the analytical results of individual samples.

The temperature history of the effluent and the volumes of water and gasoline recovered during the first pass are summarized in Figure 8. The calculated boiling point is that at which water will boil under the system vacuum applied to the vapor extraction well. In the first pass, this value was around 90°C, except when the vacuum pump was shut down (e.g. day 3). After day 25, the vacuum increased slightly because considerable steam was being extracted, and the condensation of that steam in the heat exchange system added to the applied system vacuum. The temperature of water pumped from the wells matches the boiling point curve after steam breakthrough to the extraction well, as does the temperature of extracted vapor when large amounts of steam were being extracted. For most of the first pass, however, the vapor temperature was lower due to the large screen zone pulling air in from unheated zones higher in the formation and the cooling effect of the surface compressed-air used to run the air-lift extraction pumps.

The liquid condensed from the vapor-extraction system contained both water and gasoline. Around day 10 of the operation, this condensation rate increased dramatically as steam "broke through" to the extraction wells in the lower steam zone (Figure 8). Steam flow to this zone was then redirected to the upper steam zone, which heated to breakthrough on about day 28. The condensation system utilized a flat-plate heat exchanger, removing the liquid from the vapor stream with a cyclone separator. The remaining vapor was still in equilibrium with the condensed liquid, however, so much of the gasoline remained in the vapor state and was carried to the vapor treatment system. The condensed water, often gasoline-saturated, was sent to the water treatment system along with the water removed by direct pumping (the pump

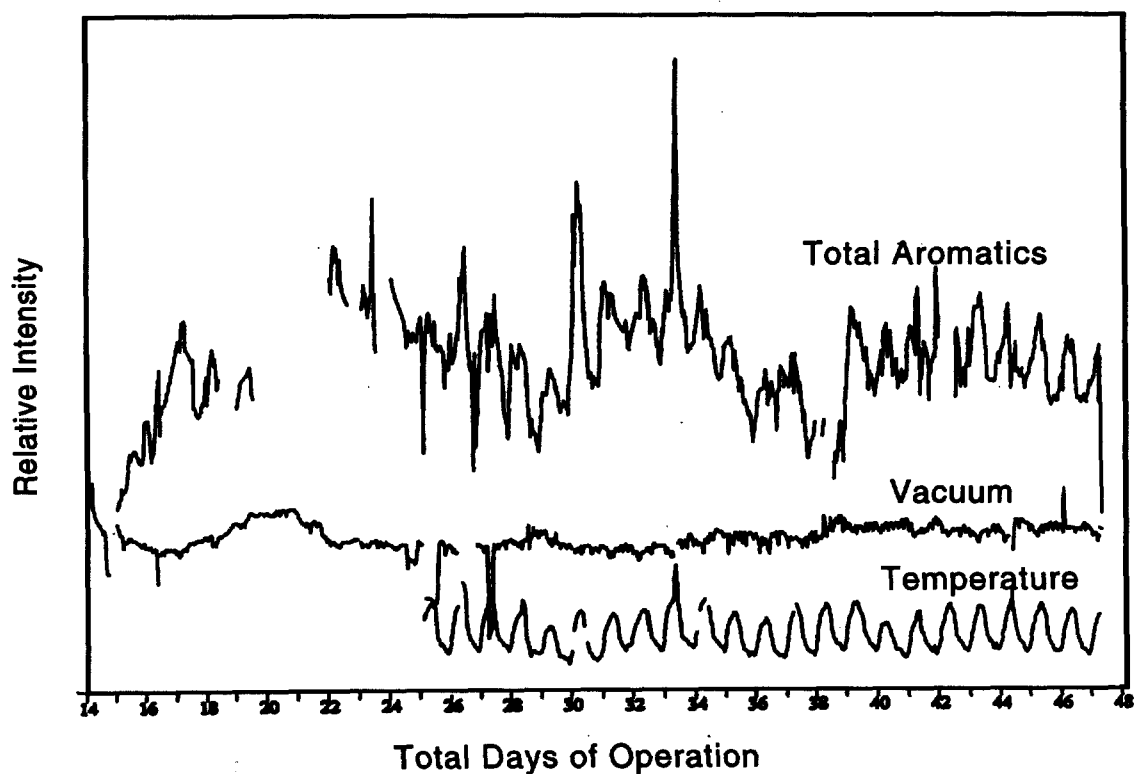
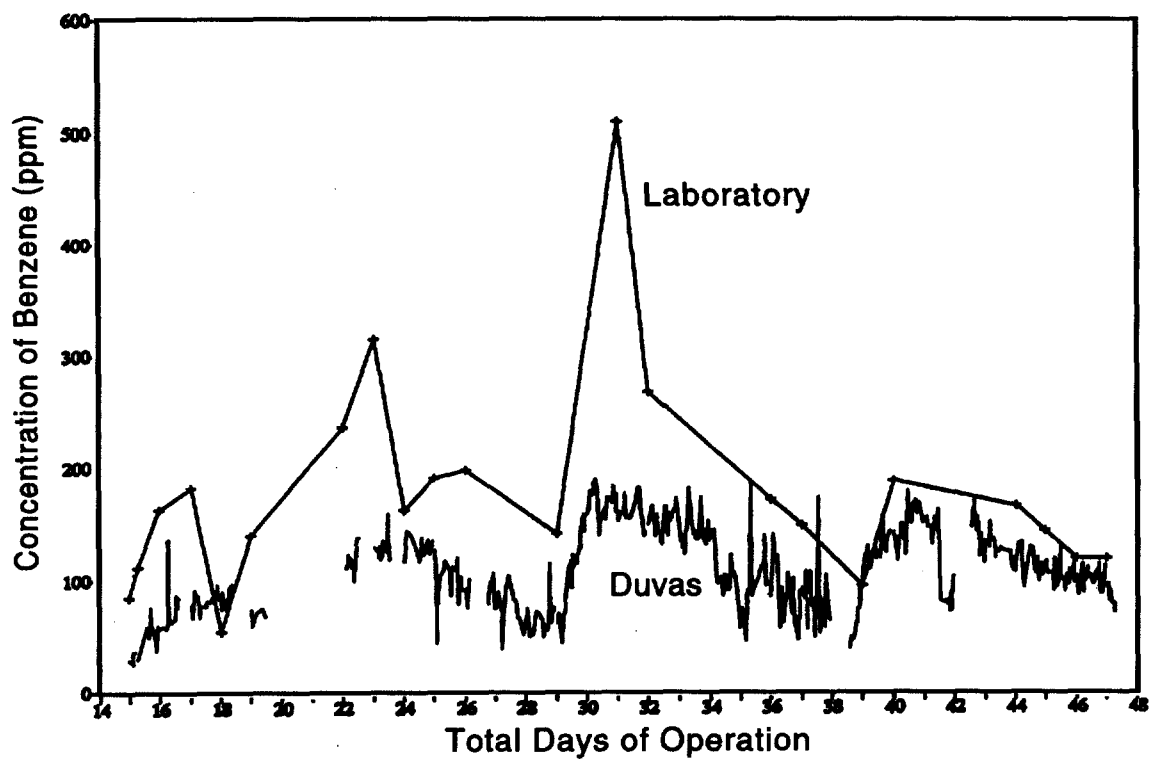


Figure 7. (a) Comparison of the benzene concentration measured by DUVAS and off-line laboratory analyses, (b) observed variations of relative total aromatic concentration from DUVAS, extraction line vacuum, and vapor temperature. Figure taken from Newmark et al., 1994b.

Temperature and Extraction Rates - First Pass

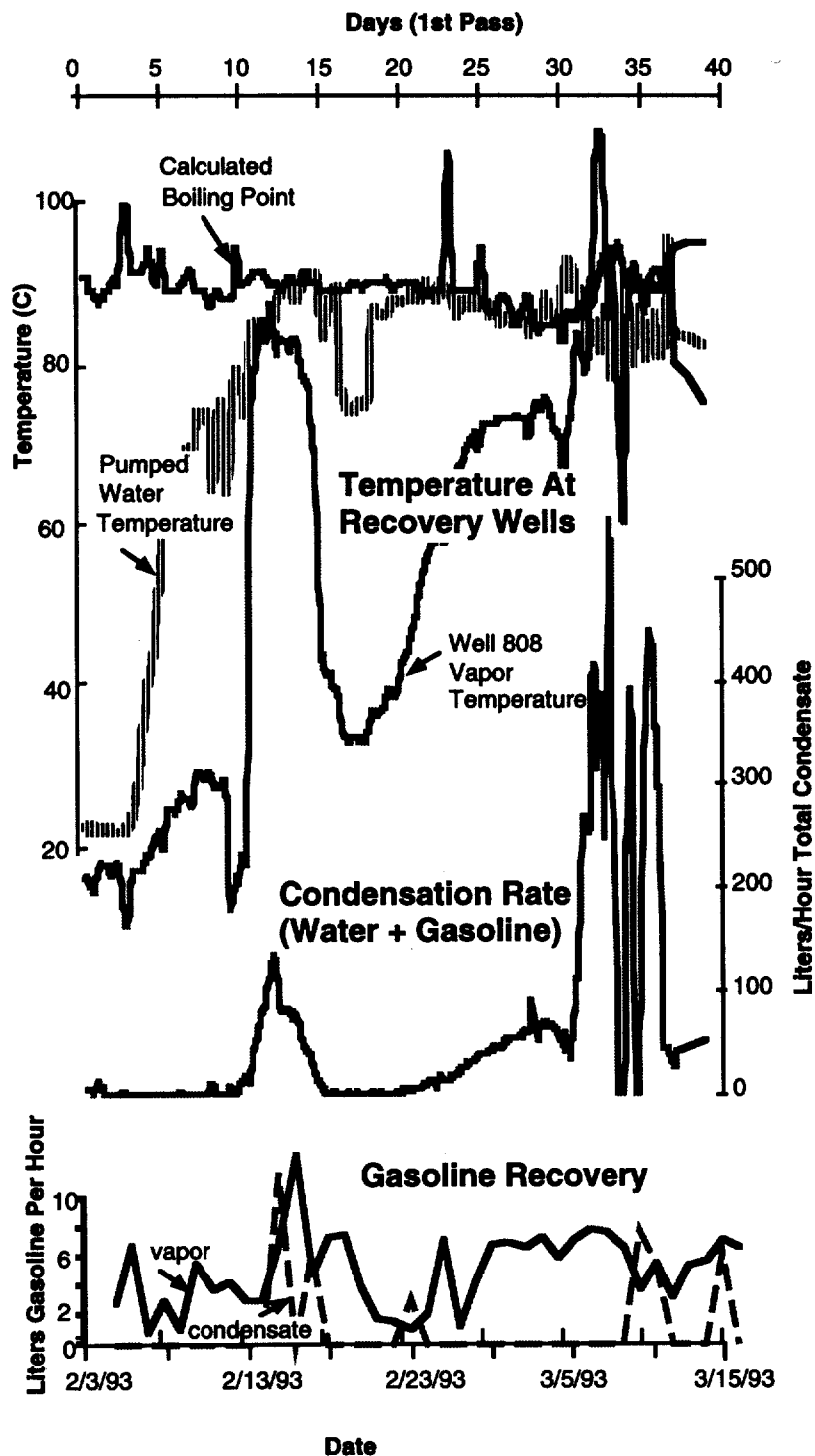


Figure 8 First pass extraction temperatures, rates of accumulation of total condensate, and gasoline recovery rates from the vapor and condensate streams. Calculated boiling points from the Steam Tables, CRC Press. Two occasions where the calculated boiling points are seen to rise above 100°C are due to pressurization of the extraction system when the carbon trailer system pump failed. The wells were quenched with cold water at that point (the vapor system was not designed to be under pressure, just vacuum). From Newmark et al., 1994a.

rate was set to equal the rate at which water was injected as steam). The majority of the product was removed in the vapor phase.

Second Steam Pass

The amount of water and gasoline vapor removed during the first steam pass (~6400 liters) was limited by the capacity of the vapor treatment system (~95 liters/day); subsequently, the vapor treatment was redesigned to increase its capacity. After a 3-month shutdown, during which the effluent treatment facility was upgraded and the in-process sampling and analysis procedures were improved, the second steam pass was conducted from May into July, 1993. The previous liquid-ring-pump-based vacuum system was replaced with an internal combustion engine system in which the applied vacuum came from the engine manifold. Thus, the applied vacuum and total vapor extraction rates were lower in the second pass, although the total gasoline removal was much higher due to the increased treatment capacity.

Extraction rates were high at the beginning of this pass, because residual heat in the soil had vaporized much of the remaining gasoline during the shutdown period. During the second steam pass, operations were conducted in a "huff-and-puff" manner, alternating steam injection and vacuum-only phases on a five- to six-day cycle (Figure 9). The extraction rate varied considerably depending on the amount of steam injected and the total vacuum applied; more gasoline was extracted when steam was not being injected and thus the vacuum effect was greater. During this pass, the average extraction rate was more than 380 liters/day of gasoline (compared to 3 liters/day for pump-and-treat).

As during the first pass, extracted water and vapor temperatures are limited to the boiling point of water after steam breakthrough to the extraction well. During the second pass, the amount (and location) of injected steam was varied, while the extraction system remained at full capacity. This resulted in a "huff and puff" operation, reflected in the amounts of extracted vapor and in the temperature variations not seen in the first pass where steam was injected continuously. On day 20, the steam recovery rate was at a maximum, and steam injection was slowed to maximize gasoline recovery. This also occurred on days 28 and 36, each time with a corresponding rapid rise in the amount of recovered gasoline vapor.

Temperature and Extraction Rate Summary - Second Pass

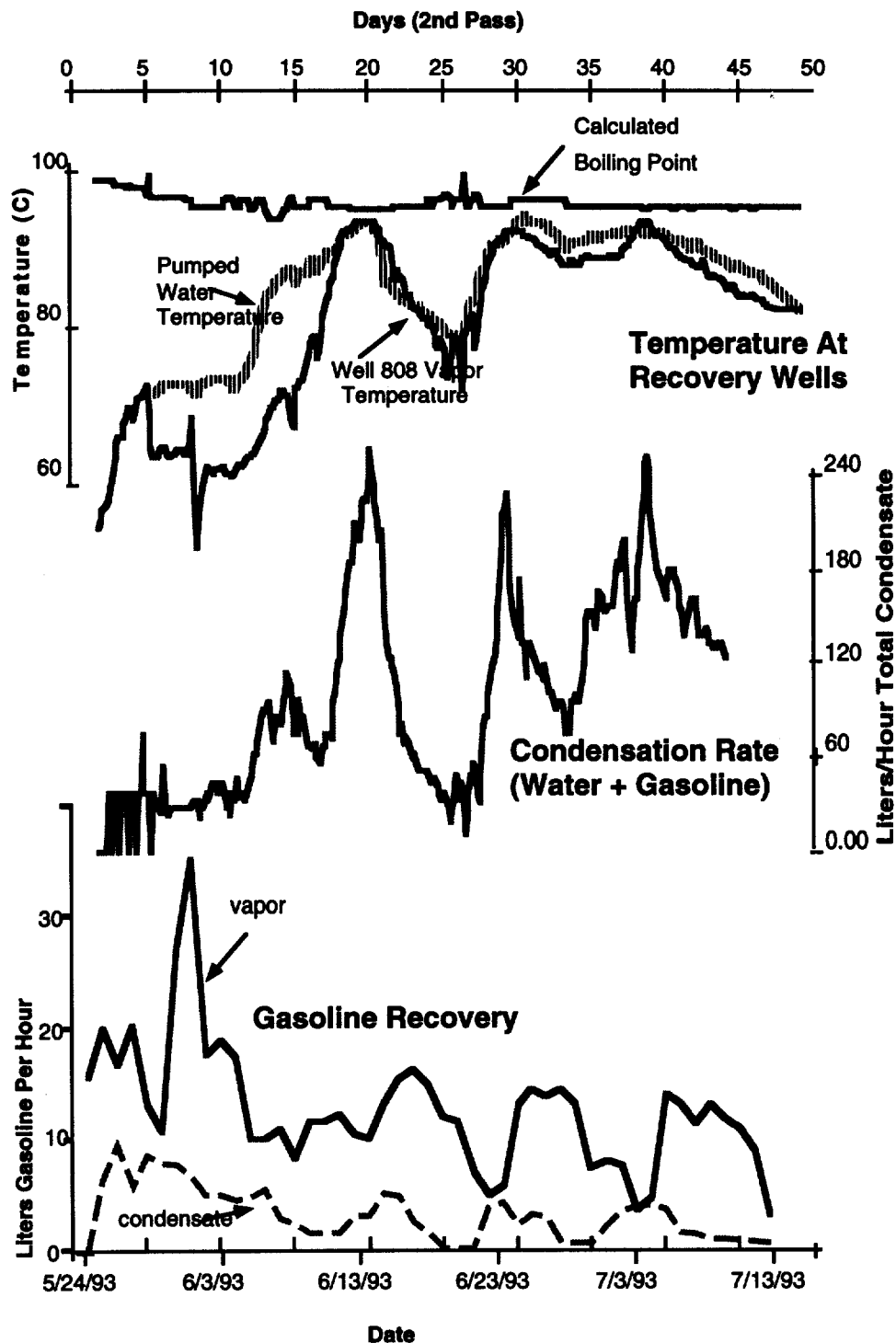


Figure 9. Second pass extraction temperatures, rates of accumulation of total condensate, and gasoline recovery rates from the vapor and condensate streams. Scaled to approximately the same time and extraction rate/temperature scales as Figure 8, although absolute values differ. Groundwater pumping began on day 5 of the second pass. From Newmark et al., 1994a.

Drillback

The second steam pass completed the experimental phase of operations. After the second steam pass, we drilled six boreholes across the treated site as close to pre-treatment characterization wells as possible, to evaluate the extent of treatment. Recovered soil samples revealed that free-product gasoline had been removed from the edges of the spill and from the zone above the water table (Figure 10). They also revealed that contamination had not been spread: gasoline concentrations had not increased in the soil outside the treatment volume. Most of the soil within the treatment volume was heated to the boiling point of water; only a thick clay layer at 30 to 34 m was cooler, having reached only 80° C in places. This "cold spot" was where the largest concentration of free-product gasoline remained, an estimated 3000 liters.

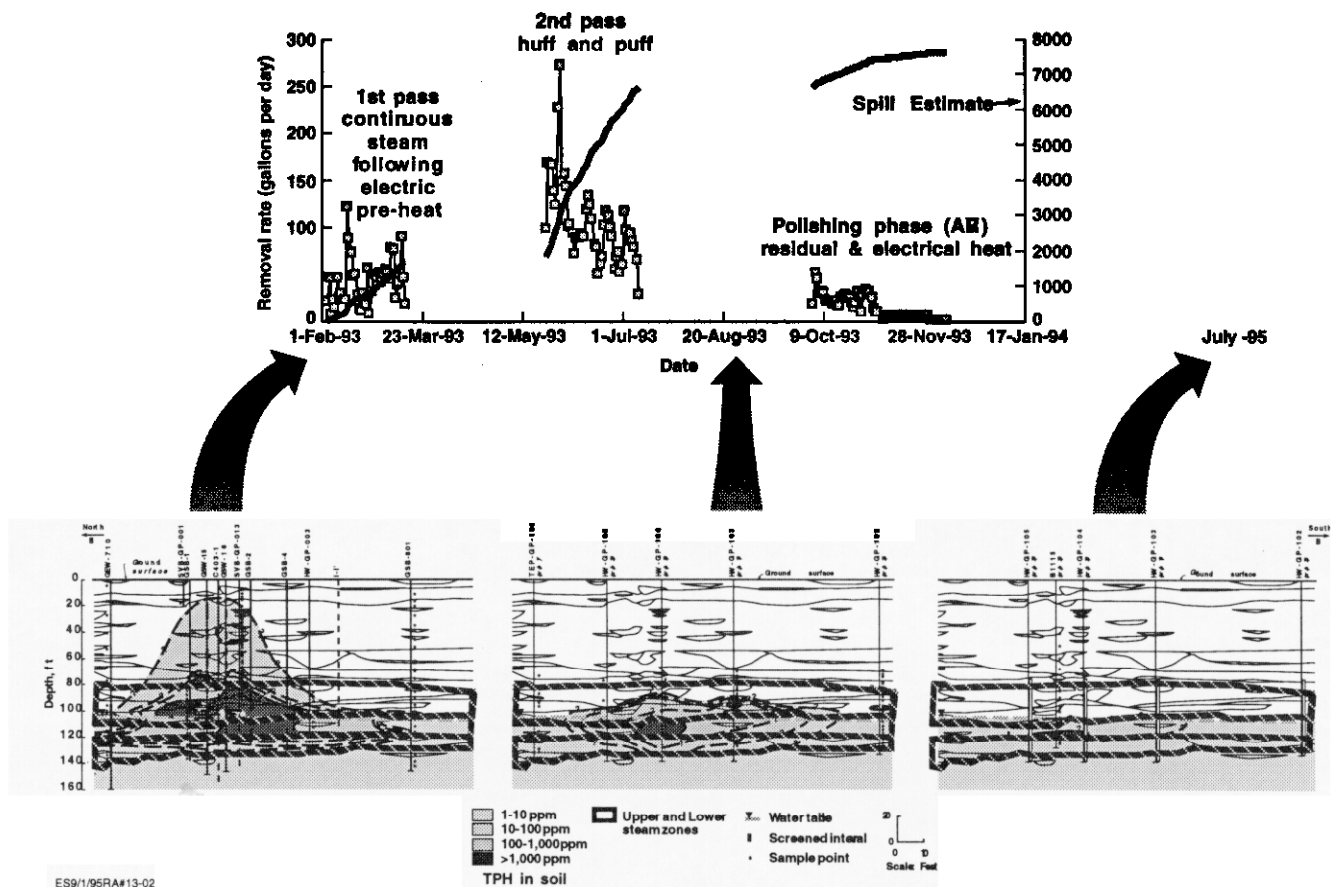


Figure 10. Daily extraction rates and cumulative gasoline recovery during the three extraction phases. Extraction rates were highest during the second phase, when extraction systems were optimized using a pulsed mode of operation. Cross sections show contaminant concentrations measured in soil samples before operations began, after the second steam pass and after groundwater extraction had ceased.

Final Heating and Extraction: the Accelerated Removal and Validation (ARV) Phase

After completing the initial experimental phase in July, we resumed extracting groundwater and vapor. The initial spike in extraction rates at this time was smaller than after the first pass. In November 1993, electric heating was applied to the remaining cool clay-rich area. The overall temperature of the treated zone rose only slightly because the extraction systems were removing much of the deposited electrical energy. When groundwater pumping and vapor extraction resumed in January, 1994, gasoline concentrations in the recovered groundwater had decreased and the gasoline vapor concentrations increased only slightly, suggesting that no significant amount of free-product gasoline remained to be volatilized. Benzene concentrations in the extraction wells were <200 ppb, down from their peak of 7000 ppb before the first steam pass. This last extraction phase removed about 3800 liters of gasoline, for a total of at least 29,000 liters removed during the three phases of the demonstration (Figure 10).

Subsequent Actions and Site Closure

In January 1994, groundwater pumping and extraction resumed at a reduced rate (nominally during working hours on weekdays), and effluent concentrations were monitored on a regular basis. Benzene concentrations in the extraction wells were less than 200 ppb from a peak of 7000 ppb before the start of steam injection. At a groundwater monitoring well within the pattern, benzene concentrations had decreased dramatically, from several thousand parts per billion before Dynamic Underground Stripping to less than 30 ppb in January of 1994. Other wells showed similar decreases. Of the six contaminants of regulatory concern at the beginning of the demonstration, five were below MCL in all wells. These factors indicate that there no significant free-phase gasoline remains in the treatment volume, although significant contamination might still lie outside the treatment volume.

In April, 1995, groundwater pumping and treating for fuel hydrocarbons ceased at the site. In July 1995, wells drilled through the treated area to a deeper, solvent-contaminated aquifer were sampled; only minor residual concentrations were detected (Figure 10). In August, 1995, regulatory approval for closure of the vadose zone vapor treatment system was received. In October, 1996 the San Francisco Bay Region, Regional Water Quality Control Board confirmed the completion of remedial action for petroleum hydrocarbon impacted groundwater underlying the area (RWQCB, 1996).

Discussion

The initial objective of this demonstration was to remove the separate phase gasoline from the treatment area. This objective was met and exceeded; Dynamic Underground Stripping lowered the benzene concentrations inside the central region to levels below those observed outside the treated area (the so-called bathtub ring of untreated but slightly contaminated water). The regulated contaminants 1,2 dichloroethane (DCA), xylene, and toluene were at or near their allowed MCLs in the treated area groundwater at the conclusion of operations (Figure 11).

The ability of Dynamic Underground Stripping to remove contaminants to such low levels in groundwater is probably indicative of the boil-off distillation mechanism described by Udell (1994). Because volatile components are generally removed from boiling water at a mass-removal rate exceeding that of the water, boiling a small percentage of the pore water can

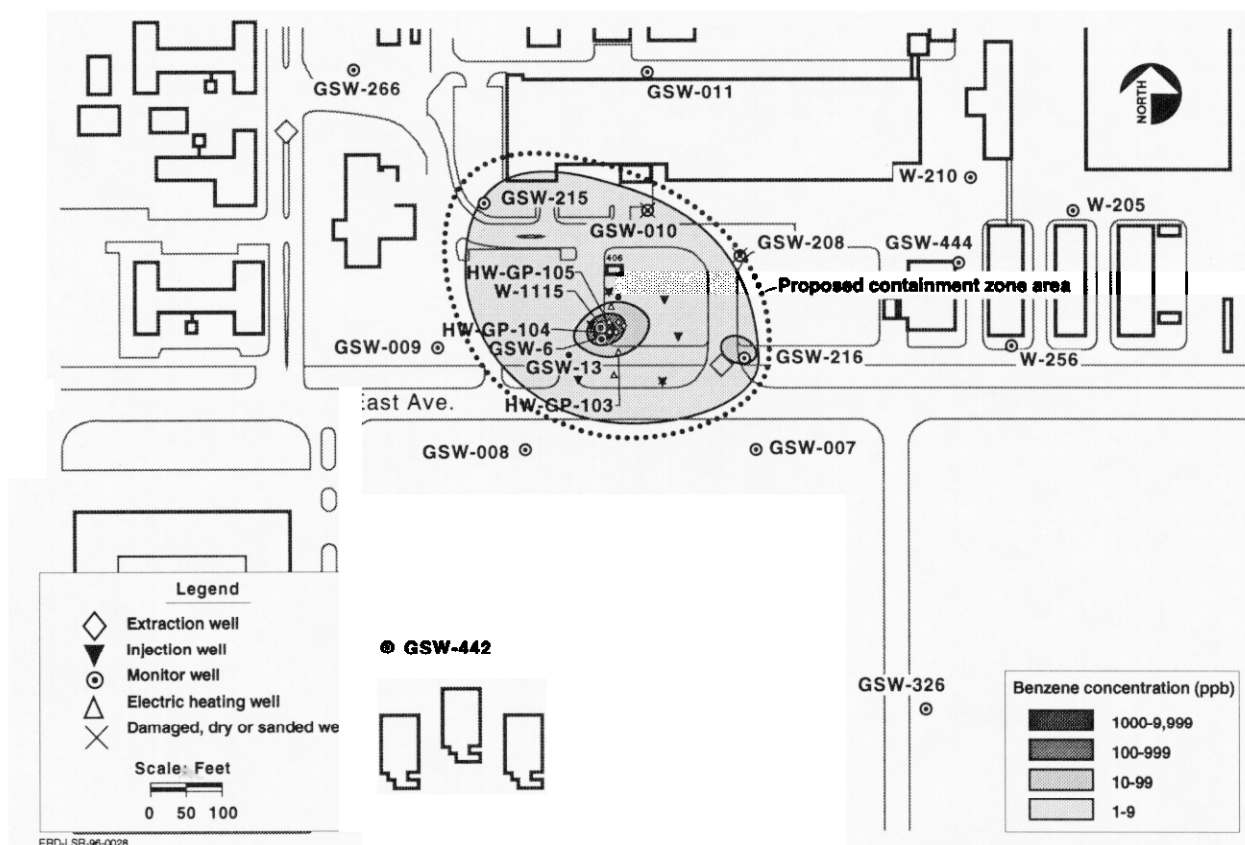


Figure 11. Maximum groundwater benzene concentration in HSN-3 (the target hydrostratigraphic zone) during the 1995 bioremediation study, following completion of vapor extraction, Dynamic Underground Stripping and pump-and-treat remediation, (from Happel et al., 1996).

dramatically reduce aqueous concentrations. Udell examines the effect as a function of boiling rate, solubility and Henry's law constants; unfortunately, solubility and Henry's law constants are not known at high temperatures for most groundwater contaminants. This mechanism may be responsible for the almost instantaneous removal of 1,2 DCA from the site groundwater and for the dramatic decrease seen in benzene relative to xylene.

Initial characterization revealed that a wide variety of microorganisms were actively degrading the BTEX components of the gasoline (Newmark, 1994a). The largest populations existed in areas where gasoline was present at low concentrations. In the capillary fringe zone, where gasoline concentrations were highest, there were low numbers of culturable organisms. Removing the separate phase gasoline should permit final reduction of contaminant levels to below MCLs. However, it was expected that thermal remediation might sterilize the soils or at least adversely affect the established microbial community. Post-test drill-back in August 1993 revealed extensive microbial communities flourishing in all samples, including those in which the soil was collected at temperatures greater than 90°C. The dominant species were no longer bacteria, but yeasts and related organisms which had been observed in small numbers before heating. Thermophiles previously identified from environments such as the hot springs at Yellowstone National Park were important members of the new community, as well as a number of other organisms apparently representing previously unidentified species. Despite the high temperature environment, McNab and others (1995, Happel et al., 1996) have shown that active intrinsic biodegradation of the hydrocarbons is occurring in the subsurface.

Conclusion

The gasoline spill demonstration clearly showed that innovative thermal methods can quickly and effectively clean a contaminated site. Not only was the separate phase gasoline removed, but the groundwater contamination was reduced to or near MCLs. Thermal treatment under these conditions did not sterilize the site, and instead led to the establishment of flourishing indigenous microbial ecosystems at soil temperatures up to 90 °C. The very positive response of California regulators, who provided quick closure authorization for the site, indicates that these methods will be accepted for use. Our research demonstration cost of approximately \$65 per cubic yard saved millions of dollars on this site, and commercial application of these methods will significantly reduce this cost.

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References

- Happel, A.M., R.W. Bainer, L.L. Berg, M.D. Dresen and A.L. Lamarre, ed., 1996.
Application for Containment Zone for the Livermore Site hydrocarbon impacted zone at
Treatment Facility F., Lawrence Livermore National Laboratory *UCRL-AR-123385*.
- McNab, W. Jr., A. Happel, P.L. Krauter, M. Reinhard, A. Spormann and V. Warikoo, 1995.
Fuel hydrocarbon biodegradation in groundwater at elevated temperatures, abstract in
Eos Transactions, 76(46), p. F189.
- Newmark, R.L. 1992. Dynamic underground stripping demonstration project, interim
engineering report, Lawrence Livermore National Laboratory, *UCRL-ID-110064*.
- Newmark, R.L (ed.), 1994a. Dynamic underground stripping demonstration project, LLNL
gasoline spill demonstration report. Lawrence Livermore National Laboratory, *UCRL-
ID-116964*.
- Newmark, R.L., 1994b. Using geophysical techniques to control in situ thermal remediation,
Proc. Symp. on Application of Geophysics to Engineering and Environmental Problems,
Boston, MA., March 27-31, 195-211.
- Regional Water Quality Control Board (RWQCB), 1996. File 2199.9026 (MBR).
- Udell, K. S., 1994. Heat and mass transfer in cleanup of toxic waste, *Advances in Heat
Transfer Research*, C.L. Tien, ed., Environmental and Engineering Geophysical Society,
Englewood, CO., pp. 195-211.